Solvent Safety

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The safe handling of flammable petroleum solvents used in the solvent extraction of oilseeds begins with the design of a new plant. The areas requiring strict attention deal with receiving, storage and handling the solvent. Strict operating procedures should be prepared and followed. Employees must constantly be made aware of the hazards involved in handling flammable solvents. Recognized groups have outlined the requirements in both design and operating practice which will help managers and superintendents insure and enhance their plant operating safety.

Hexane (C_6H_{14}) is a paraffinic hydrocarbon and a colorless liquid with an obvious odor which has been described as good to pleasant. Its specific gravity is ca. .685, or slightly less than 5.6 lb/gal. It has a boiling range of 150–156 F (65.6–68.9 C). Unfortunately, these are the only benign characteristics of this liquid. Its open cup flash point, defined as the temperature at which the vapors of a volatile liquid mixed with air spontaneously ignite, is -14.4 F (-25.8 C) and a closed cup flash point of -7 F (-21.7 C). The rate of flame propagation in an open air vapor conflagration is more than 15 ft/sec (4.6 m/sec). In an open air vapor explosion, 20 gal of hexane has an equivalent explosive force as 1 lb of TNT. This statistic means that the amount of hexane normally stored at an oilseed processing plant, when mixed with adequate oxygen for combustion, could level a normal-sized city block.

Why would we wish to subject ourselves to close proximity to such a dangerous material? If anyone were to tell me that he has no concern at all about working around hexane, I would question his mental competence. Even before the first fire or explosion occurred at a plant using hexane as the solvent, people were exploring the range of available solvents for one which is nonflammable and functional for the extraction of vegetable oils. A variety of solvents has been tried in the extraction of vegetable oil. Trichloroethylene (TCE) is nonflammable, has a reasonably high boiling point, and does a superb job of extracting oil from oilseeds; however, it has one significant drawback. During the extraction process, it participates in a chemical process which leaves the resultant meal with certain constituents which are toxic to animals. Methylene chloride also does an excellent job of extracting vegetable oil and does not have the toxic effects of TCE, but has a boiling range of 90–100 F (32–37.8 C), which makes it unmanageable in warm climates.

Normal hexane has the best compromise of solubility, low latent heat of vaporization and boiling range, and until another solvent which is nonflammable meets these requirements and is approved by the appropriate agencies of government, we will continue to deal with hazardous, flammable solvents.

For ease of demonstrating some of the safety procedures, I would like to review the basic elements of combustion. There are three elements necessary to produce normal combustion. These are: fuel, oxygen and heat. The objective of most safety procedures and standards in solvent extraction plants is designed to prevent the combination of these three conditions. If at all possible, the attempt must be made to prevent a combination of even two of these elements.

The *National Fire Protection Association Bulletin #36* (National Fire Protection Association, 470 Atlantic Ave., Boston, MA 02210) should always be on hand to remind you of information you may not remember.

A method of isolating fuel (hexane) from oxygen is to keep the hexane confined in the vessels which were designed for this purpose. This is done by maintaining effective gaskets and seals on all vessels and pumps. A regular maintenance procedure should involve checking these gaskets and seals and when they are removed for maintenance, they should not be reused or replaced. When the seals separating the oxygen from hexane during maintenance procedures are broken, the protective barrier separating these two elements of combustion is gone. Thus, prior to removing this barrier, hexane should be purged from the vessel.

There is a variety of heat sources that must be prevented from contacting hexane. The most obvious of these, of course, is open flames. For this reason, boilers, internal combustion engines and smoking is prohibited within 100 ft of a solvent extraction plant. Within this same 100-ft area, electrical power cables and switches must be within explosion-proof enclosures. This definition of explosion-proof does not imply a total prevention of hexane coming into contact with electrical sparks, but means that, should an explosion occur, it will be confined to the explosion-proof enclosure. Static electricity also is a source of heat for the combustion triangle. Static electricity can be produced in at least three ways. It can be mechanically induced by rotating machinery, personally produced by wearing of improper clothing and shoes, or—the one source over which we have no control—it can be weather-induced. The precautions which can be taken against mechanically induced static electricity are the proper grounding of all machinery, and the prohibition of belt drives in the extraction area. For the weather-related static electricity in the form of lightning, lightning rods and grounding of the equipment and building to a common point offers the most protection. Training of personnel is the best way to avoid the static electricity produced by people. It is recommended that synthetic fiber clothing not be worn, i.e., that clothing be made of cotton. Footwear should be of a type with no exposed steel nails, and it is also recommended that rubber-soled shoes not be worn, because these insulate the wearer so that a charge will accumulate on his body.

This is not a large number of rules to remember; let us then see how they can be practically applied.

The first danger is in the receiving, unloading and storage of hexane. The same rules apply, whether you receive hexane by truck or by railcar. In the hexane receiving area, signs should be posted prohibiting open flames within 100 ft of the point of unloading. Both the tank and the truck or railcar must be grounded to a common point. The truck or railcar wheels should be blocked and the brake set to prevent any movement. The truck motor must be turned off during the unloading and the driver should not leave his vehicle unattended. Of utmost importance during this period is that a responsible supervisor be present to insure that these procedures are enforced during the entire unloading operation. After this unloading operation, the solvent is once again confined with a steel wall as a barrier separating the hexane and oxygen.

The next dangerous period during which it is difficult to separate the elements of combustion is in the shutdown process. A detailed analysis of shutdown procedures is

pointless at this time, because all solvent extraction installations are different from each other in one way or another. The objective of an orderly shutdown is to remove the hexane from process vessels, and transfer it once again to a safe storage point. This storage point may be in a vessel within the extraction plant, if it is to be a short duration shutdown, or back to the hexane storage tank outside of the plant if the shutdown is to be of long duration.

In the shutting-down process, vessels are emptied in an orderly manner by first stopping the feed of raw materials to the extractor. The extractor continues to run until raw material has been extracted and desolventized and moved out of the extraction plant. Because most extraction systems are the countercurrent type, solvent and miscella cannot be removed from the extraction vessel until after the spent materials are completely processed. After the spent material is removed from the extractor, the supply of fresh solvent is stopped. The pumping of the various stages continues until the wells or containers for these stages are emptied, at which time the appropriate pumps are stopped. While the extractor is being emptied and afterward, the distillation and solvent recovery systems continue to run until all miscella has been evaporated, and the solvent condensed. This is the point at which the decision is made for purging either the entire plant or only the vessel on which work is required.

At this point, flammable vapor should be mentioned. We are all familiar with the flooded carburetor of a car. This is the case where the proportion of air and fuel is too rich to make an explosive mixture. The opposite case also can occur when there is too little fuel in the fuel and air mixture for explosion to occur. The same is true of the mixture of hexane and air. This explosive mixture is the range from 1.1 to 7.5% by wt. These percentages are referred to as the lower explosive limit and the upper explosive limit, or LEL and UEL.

Prior to opening a vessel containing hexane in liquid or vapor form, the mixture is well above the upper explosive limit and approaches 100% concentration. The purging of vessels (particularly the extractor) is designed to keep this mixture outside the explosive limits. We can do this by using another gas which is not flammable to displace the hexane vapor, prior to the admittance of air. Nitrogen and carbon dioxide, when put into a vessel, will displace the hexane vapor from that vessel. Once this is accomplished, air can be admitted, and the hexane vapor will have been removed from the vessel having never entered the explosive range.

This same procedure can be used in reverse during start-up by displacing air with the inert gas before admitting hexane to the vessel.

Heat sources of all types are used in maintenance, e.g., welding equipment, torches and steel tools. For this reason, absolute control is required and it is recommended that a system be established whereby these tools are not permitted in the extraction area without written authorization of the supervisor. This authorization should be given only after a thorough inspection is made and the area has been tested and shown to be free of hexane vapors. For light maintenance in areas which are not free from hexane vapor, spark-proof tools made of brass or aluminum alloy must be used.

Visitors to a solvent extraction installation should be strictly controlled. Visitors must certainly be advised of the danger of working around hexane, and must leave any matches or other smoking materials in a safe place prior to entering this area. Visitors should receive badges or other identification so that workers in the area will know they are authorized. Workers must also be instructed to challenge anyone visiting who does not have this badge.

It is possible that all of these precautions may fail and a fire will start. There is a variety of systems for fire protection. I am not an expert on any of them, and, thus, will not offer my opinion on which is the best. I suggest, however, that whichever system is installed, its main purpose is protecting people, not equipment. The systems are heat-activated, and when activated, may put out a small fire, but mainly will offer protection for people within the building and allow adequate time for escape. Whichever system is used, it is vital that all people working in the area be thoroughly familiar with the operation of the system, so that if they become aware of a fire before it is sensed by the system, they may activate it.

Fire fighting equipment is equally important, because most solvent extraction plants are located in relatively remote areas for aesthetic considerations. All people working in this area must be familiar with the location and operation of hydrants and extinguishers so that they may, once they are safe from the fire, make every effort to extinguish it. This should be part of a regular training program for employees.

Hexane vapor has a characteristic that is quite often ignored, even by those very used to working with hexane. That is, hexane is dangerous to breathe in high concentrations. Areas with high concentrations of hexane are very intoxicating, and because it is more dense than air, hexane displaces air which can lead to asphyxiation in people breathing the vapors. For this reason, when it is necessary to work in areas of high concentration, the workers should be supplied with a portable air supply, or a mask and hose connected to an outside air supply. This alone is not a sufficient precaution, because the equipment may malfunction. Also, the worker's judgement cannot be relied upon because hexane is an intoxicant and will affect his reasoning. Thus, it is mandatory that an observer outside the vessel constantly be present to observe the worker or workers inside the vessel and determine if a dangerous condition exists and then go for help, if necessary.

Preventing the combination of the three elements of combustion is simple enough to master. However, the numerous points at which this combination can occur make the job complicated. For this reason, a regular system of inspections and reporting must be implemented. In addition to this regular reporting system, a safety committee within the plant is suggested. This committee could have rotating positions, so that all employees have an opportunity to become familiar with and feel a personal responsibility for their own and their coworkers' safety. Meetings of this committee should be held on a monthly basis and minutes of the meeting should be published for all employees to read. Recommendations of the committee for improving safety standards should carry high priority with the management of the plant, and observations of safety violations should be dealt with immediately.

REFERENCES

1. Gugan, K. "Unconfined Vapor Cloud Explosions," Gulf Publishers, 1979.
2. "Fire Protection Manual for Hydrocarbon Processing Plants," edited by C. Vervalin Gulf Publishers, 1974.
3. "Solvent Extraction Plants, 1978," National Fire Protection Association, Boston, MA, 1978.